PREPARATION OF SOLID CATALYST SUITABLE FOR BIODIESEL PRODUCTION

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Abstract

The heterogeneous esterification reaction of oleic acid becomes one of the most significant reaction in the field of the production of the biodiesel from high free-fatty acid sources.

NaY zeolite has been prepared from local available Iraqi kaolin clay. Characterization by XRD shows that the prepared catalyst was NaY zeolite. The XRF results show that the prepared NaY zeolite has 2.4 silica to alumina ratio and 12.8 wt. % of Na_2O in its structure. While, the surface area was 154 m^2/g and the volume of pore was 0.26 cm^3/g.

The prepared NaY zeolite was tested as a catalyst in esterification of oleic acid. The higher conversion obtained was 78%. The promoted NaY zeolite by copper cation improve the amount of the converted oleic acid to reach 86%.

Key words: esterification, biodiesel, heterogeneous catalyst, solid catalyst.

Introduction

There is an increasing interest in global warming and resources depletion due to the high fossil resources consumption and there has been focusing on this topic in recent years. Resources depletion and global warming have become main global issues. Using renewable sources of energy such as bio fuels (biodiesel) can help in solving this problem (Hameed *et al.*, 2009).

Sources of the renewable energy such as solar (photovoltaic and thermal), biomass, wind, hydro, hydrogen and geothermal will play a significant role in future. It is expected that in (2025) about half energy supply of the worldwide will obtain from renewable energy, and electrical production from renewable energy sources will be larger than (80%) of the entire global electrical supply (EWEA, 2005).

Exchange the fossil fuel by using biodiesel fuel is modern possible alternative as the source of energy particularly in the transportation sector. The esterification of free fatty acids can be produced biodiesel fuel, the free fatty acids are found certainly in animal fats and vegetable oils. The prospect of using oil of vegetable as energy source was suggested by Rudolph Diesel in (1892) (Zubir, 2009). Oleic acid is considered the typical feed to esterification reaction because it is the main component of vegetable oils and many fats (Cardoso *et al.*, 2008).

Examined of catalyst for the transesterification are either bases or acids, both heterogeneous and homogenous, or they are enzymes (Serio *et al.*, 2008).

Conservatively, using traditional liquid base catalysts to produce commercial biodiesel (Meher *et al.,* 2006). But, there is significant impetus for the substitution of liquid by solid bases for the following causes : corrosiveness, intensive of energy/catalyst separation and the costs associated with the neutralized caustics or spent (Zhang *et al.,* 2003). Thus, the use of heterogeneous catalysts could allow the design of an efficient, continuous process and better the biodiesel production economics. In addition, the use of heterogeneous catalysts permits a more environmentally friendly process to be used for production of biodiesel (McNeff *et al.,* 2008). Moreover, the use of heterogeneous catalysts do not generate soups during neutralization of free fatty acid (Vicente *et al.,* 2004), that simplifies the separation and purification (*i.e.*

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post treatment) process. Due to these advantages, study on the esterification or transesterification reaction using heterogeneous catalysts for production of biodiesel has developed over the past decade (Islam *et al.,* 2013).

Biodiesel

Biodiesel is defined as a fuel derived from renewable sources, composed of mono-alkyl esters of long chain fatty acids such as animals fats and vegetable oils (Math *et al.,* 2010).

Biodiesel has acquired international concern as alternative fuel source because advantages like low carbon monoxide emission, no toxicity, high degradability, unburned hydrocarbons and particulate matter (Zabeti *et al.,* 2009). Biodiesel is an alkyl esters mixture, include (10-15%) oxygen by weight and sulfur free, it can be used in engines of conventional compression ignitions, that require nearly no transformation. Also, biodiesel can be used as fuel and heating oil (Sharma *et al.,* 2011).

Many vegetable oil types such as palm, palm kernel, canola, count oil and sunflower have been inspected as a feed stock for biodiesel production. The major characteristic interesting production of biodiesel from these feed stocks is the large price of combustible oils of vegetable compared to that of fossil based diesel fuel. Therefore oils of nonedible such as oils of cooking waste are selected for production of biodiesel because their low price (Al Zuhair, 2007). Modern creation biodiesel wants to gain raw material from algae and other renewable feed stock, that will supplied sustainability of the sum total production of biodiesel process required to sufficiently justify the industry of biodiesel (Mushrush *et al.,* 2001).

These truth drive biodiesel to reduce exhaust emissions than diesel fuel due to complete combustion. Moreover, biodiesel has a higher Cetane number than diesel fuel, flush point, viscosity, pour point and density. Using biodiesel can support less the world's dependence on fuels of fossil, and it causes important environmental advantages. In addition, the content of energy or the net biodiesel calorific value is approximately (12%) lower than that of diesel fuel on a mass basis. For example, using biodiesel fuel instead of the conventional diesel fuel meaning fully decreases the emissions of exhaust such as the carbon dioxide of the overall life circle, sulfur oxides (SO_x), carbon monoxide, volatile organic compounds, unburned hydrocarbons (HC) and particulate matter (PM). Biodiesel emits reduce exhaust emissions of tail pipe compared to the diesel fuel, about (50%) reduce in emission of PM, about (50%) minimum in emission of CO and nearly (68%) lower in emission of HC. Moreover,

since biodiesel fuel is a sulfur-free fuel, it receives approximately (99%) lower emission of SO_x than the fuel of diesel. Nearly (10-15%) higher of oxide nitrogen (NO_x) produced from most of the biodiesel who fueling with (100%) biodiesel. According to the feed stock plentiful availability in the local country, the several feed stocks are focused in the production of biodiesel (Basha and Gopal, 2012).

Biodiesesl feedstock

All animals fats and vegetable oils can be utilized as a feed stock for the production of biodiesel. Most of these fats and oils have an identical chemical composition, they contain different quantities of individual fatty acids and triglycerides. The main fatty acids are those with (16 and 18) carbons a chain length, while the chain could be unsaturated or saturated (Soelaret and Vandamme, 2009).

Oils and fats are primarily hydrophobic, water-insoluble substances in the plant and animal kingdom which are comprised of three moles of fatty acids and one mole of glycerol and are generally known as triglycerides (Sonntag, 1979). Biodiesel contains fatty acids with several levels of un-saturation, which are affecting the properties of the biodiesel produced.

Content of free fatty acid (FFA) is the quantity of fatty acid (wt.%) in oil that is not linked to molecule of triglyceride. Breakage of long carbon chain can be obtained by heating oil and formation of FFAs. Through the process of transesterification, alkali react with free fatty acids, and form soaps and water both of that must be eliminated during the process of ester purification.

Furthermore, FFA attracts water due to their hygroscopic nature.

The oil energy content is the calorific content. The biodiesel energy content depends on the feed stock oil energy content, commonly fuels with more unsaturation have a less energy (on a weight basis) whereas fuel with higher unsaturation have greater content of energy.

Impurities, un-saponifiables and water are the amount of filterable solids such as (particles of food, fragments of bone or other solids), other non-triglycerides in an oil that cannot be converted to mono alkyl fatty esters by transesterification or esterification. Therefore, impurities, un-saponifiables and water must be removed or during purification of ester before production of biodiesel (Karmakar *et al.,* 2010).

Catalysts types for trans-esterification and esterification reaction

The reaction is easiness with a convenient catalyst (Wang *et al.,* 2009). If the catalyst continuous in an

immiscible liquid, gaseous or solid (*i.e* different phase) to which of the reactants the process is known heterogeneous catalytic process. But, if the catalyst continuous in the same (phase) liquid to which of the reactants through trans-esterification it is a process of homogeneous catalytic (Al Zuhair, 2007).

Catalysis of homogenous alkaline

Basic or alkaline compounds are until now the mot generally used catalysts for biodiesel production. The major advantage of this form of catalysis over transesterification is the more rate under mild conditions in relatively low reaction times (de Vrije and Claassen, 2003). It attains a high yield and purity of biodiesel production in (30 to 60) minutes (Wang *et al.,* 2007). Furthermore, alkaline catalysts are lower corrosive to industrial equipment (Soelaret and Vandamme, 2009).

The major technology drawback is the sensibility of main catalysts to free fatty acids included in the material of the feedstock. This means that transesterification of alkali-catalyzed optimally operate with less acidic, high-quality vegetable oils, that are however higher costly than waste oils (Soelaret and Vandamme, 2009). In this process only vegetable oil of well-refined with lower than (0.5 wt.%) free fatty acid (FFA) can be used as the reactant. Thig high raw material cost is the main block to its commercialization (Wang *et al.,* 2007). If materials of low cost, such as waste fats with a more quantity of free fatty acids, are to be processed by alkaline catalysis, pre-esterification or de-acidification (Soelaret and Vandamme, 2009).

Catalysis of homogenous acid

Acid catalysis shows the significant advantage of free fatty acids included the oils and fats and is therefore particularly suitable for the transesterification of highly acidic fatty materials (Soelaret and Vandamme, 2009).

Therefore, transesterification of acid catalyzed is generally far slower than reactions of alkali-catalyzed (Minnan *et al.,* 2005). A moreover disadvantage of acid catalysis by higher reaction temperatures is a raised unwanted secondary products formation, such as di-alkyl ethers or glycerol ethers (Van Andel *et al.,* 1985).

Due to high temperatures required and the slow rates of reaction catalysts are only used for esterification reactions. Thus for fats of animal or oils of vegetable with quantity of free fatty acids over approximately (3 wt.%) two strategies are possible. The free fatty acids can either eliminated by treatment of alkaline can be esterified under acidic conditions before reaction of alkaline catalyzed transesterification. This so-called pre-esterification has the advantage which before to the most

free fatty acids trans-esterification are already converted into FAME, therefore the overall yield is much high (Soelaret and Vandamme, 2009).

Enzymes as catalyst

The metallo-organic or organic catalysts presented so far, therefore the use of lipases are enzymes, that catalyze both the synthesis of ester bonds in glycerol esters and the hydrolytic cleavage (Islam *et al.,* 2006).

As compared to other catalyst kinds, biocatalysts have many advantages. Biocatalysts allow conversion under pressure, pH and temperature conditions. Neither the glycerol phase nor the ester product has to be purified from main soaps or catalyst residues. Which means that high-quality glycerol can be sold as a byproduct, phase separation is easier, and environmental problems because alkaline waste water are removed (de Vrije *et al.,* 2002).

Because enzymes tolerate free water and fatty acid contents, facilitating easy purification of glycerol and biodiesel lead to use of enzyme catalytic production of biodiesel has attracted much attention in recent years. Therefore, enzymatic transesterification could not be commercialized for production of biodiesel because the large cost and high residence time. Some researches show which the lipase in an enzyme catalyzed process is very sensitive to methanol, so the methanol in the reaction system should be protected at very low concentration to ensure the activity of the enzyme (Dizge *et al.,* 2009).

Heterogeneous catalysis

Heterogeneous catalysts now being attempted comprehensively for synthesis of biodiesel. These catalysts are poised to play a significant role in future for production of biodiesel at industrial level (Mushrush *et al.,* 2001).

The production of soup can be obtained from the use of homogenous catalysts. Furthermore, the catalyst is depleted in the homogeneous process, thus, decreasing the effectiveness of catalytic. This gives an excess in the gels formation and viscosity. In addition, the catalyst removal process after reaction is strictly speaking difficult and a high quantity of waster is generated in order to clean and separate the products, that raises the overall process cost (Taguchi *et al.,* 1994).

Glycerol produced during transesterification of homogenous catalytic is of goodness and needs purification distillation and lengthy process (Canakci and Van Gerpan, 2011).

The end products cost of glycerin and biodiesel increases because all these processing. Furthermore, the process of homogeneous base catalyzed transesterification

faced problems to treat various feed stocks. On other side, process of heterogeneous catalytic transesterification conquers these problems due to ethanol or methanol does not mix with catalyst of solid heterogeneous. It is comparatively easy to detach the glycerol and biodiesel from the catalyst (Singh chouhan and Sarma, 2011).

The major advantages of approach depicted as the high quality production of glycerol and no required for disposal of salts generating from the catalyst. While, the inclusive advantages of economic have to be prepared in long-term running.

Transesterification of the heterogeneous catalytic is contained under Green technology because the flowing imputes (Juan *et al.,* 2011): glycerol separation from biodiesel is much easier, the catalyst can be reused and there is very less or no quantity of wastewater generated during the process.

Triglycerides is converted into biodiesel slowly by using heterogeneous catalyst, but generated biodiesel is a very reasonable economic way because the catalyst reusability for both processes, e.g. continuous and batch (Viriya-empikul *et al.,* 2010).

Further advantage with catalyst of solid based is the lesser depletion of catalyst. According to studies, for producing (8000) tons of biodiesel, (88) tons of sodium hydroxide may be needed (Mbaraka *et al.,* 2006), whereas for production of (100.000) tons of biodiesel only (5.7) tons of solid supported (MgO) is sufficient (Dossin *et al.,* 2006).

Heterogeneous catalyst shows simplest production process, develop quality of product, and decrease toxicity and corrosion problems. Moreover, it can be used for feed stock with low quality, that includes high (FFA) (Mat *et al.,* 2012).

Zeolite

Zeolite are solids of microporous crystalline with well-known structures. Commonly, Zeolite include aluminum, silicon and oxygen in their framework, other molecules and water within their pores. Several exist naturally as minerals, and others are synthetic, and formed commercially for fixed uses (Bell, 2001).

Zeolite Structure

Zeolite are compounds of three-dimensional crystal line, are construct from (AlO_4) and (SiO_4) tetrahedral (Smith, 1976), a knowing characteristic zeolites is which their structures are made up of 4-linked atoms network. One path of thinking concerning this is in tetrahedra terms with oxygen atoms at the corners and atom of silicon in the middle, these tetrahedral can then connected with

one another by their corners (Smith, 1976). Fig. 1 shows zeolite structure.
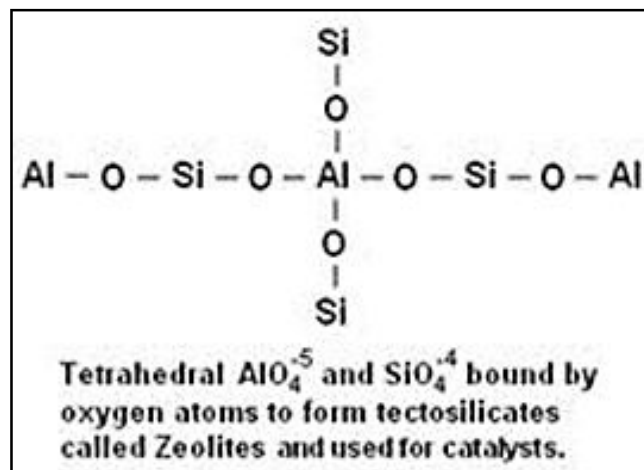
Zeolite properties

Fig. 1. Zeolite structure

These materials have three characteristics which make them deserving of a separate category and unique.

First they are highly crystalline with well-defined structure (Hala, 1971). Second, ions within the cavities are easily to exchange with a large number of multivalent ions (Hilditch and Hall, 1937). Third, ions introduce into cavities through ion exchanges have separate activities of their own (Weitkamp and zeolites, 1999).

Some individual zeolites properties are micro-porosity, cages or pore channels, large internal area of surface, uniform pore, high thermal stability nontoxic and environmentally safe (Chorkendroff, 2003).

Application of Zeolites

Zeolite have active surfaces, owing to the combination of (Al^{3+}) on sites where usually a (Si^4) pores crystalline system, enables many zeolites applications, such as (Chorkendroff, 2003).

- Ion exchange : zeolites are builders in rinsing powder, where they have progressively exchanged phosphates to link calcium. Calcium and, to a lower range, magnesium in water are replaced for sodium in zeolite A. This is the highest zeolite applications today. Zeolites are basically nontoxic and pose no environmental hazard. Zeolite are as well used in toothpaste, again to connected calcium and inhibit plaque.

- Adsorption : in separation and purification, drying. Can be absorbed zeolites up to (25%) of their weight in water.

- Catalysis : Acidic sites of zeolites which are catalytically effective in several reactions of hydrocarbon. The pore only permits molecules which are small enough to enter,

therefore, it impacts the reactions selectivity by excluding both formation and participation of molecules which are very big for the pores.

Materials and methods

Materials

All materials used in this work obtained from local markets

1- Kaolin : The clay of kaolin is obtainable locally in the (Al-Dewekhala Quarry) in (Al-Anbar) area, it was provided from Geological surveying and mining. It was used as a raw material for the catalyst production. Table 1 shows the kaolin chemical analysis.

2- Sodium hydroxide for titration (B.P.1968 M. Wt. 40).

Table 1: Chemical analysis of Iraqi Kaolin.

Component	SiO_2	Fe_2O_3	AL_2O_3	CaO	L.O.I	Na_2O
Wt %	49.64	1.72	34.05	1.10	12.28	0.46

3- Sodium silicate (Na_4SiO_3), (Supplied by BDH Limited Pool England).

4- Copper chloride ($CuCl_2$).

5- Oleic acid : The oleic acid specific gravity is (0.895).

6- The specific gravity of ethyl alcohol is (0.7692), (88 to 90 wt.%).

7- Phenolphthalein (as indicator).

Equipment

The devices used in the production of zeolite catalyst were jaw crusher, magnetic stirrer heater, programmable furnace, vacuum pump, electric oven, electrical balance (Sartorius/ BP3015 (max 3038)) and electric oven.

The equipment used in the esterification reaction were (heat flat magnetic stirrer : Stuart (CB 302)/USA), reflux condenser, centrifuge : Griffin and George Loughborough/ Britain). Fig. 2 shows the schematic diagram of the reactor.

Catalyst preparation

1- Kaolin particle size less than 75 μm that obtained by the sieve.

2- Particles of Kaolin was mixed with (40%) solution of NaOH using (Kaolin/ sodium hydroxide = 1/1.5) and then fused at temperature (850°C) for three hours.

3- 63 gm of sodium silicate and 50 gm of fused Kaolin were mixed in deionized water (500 ml) under fixed stirring at temperature (50°C) for one hour using electric stirrer shown in fig. 2.

4- The slurry at pH of (13.3) was putted in glass jar (1000 ml) and subjected to aging at 50°C for (24) hours in a programmable electrical furnace.
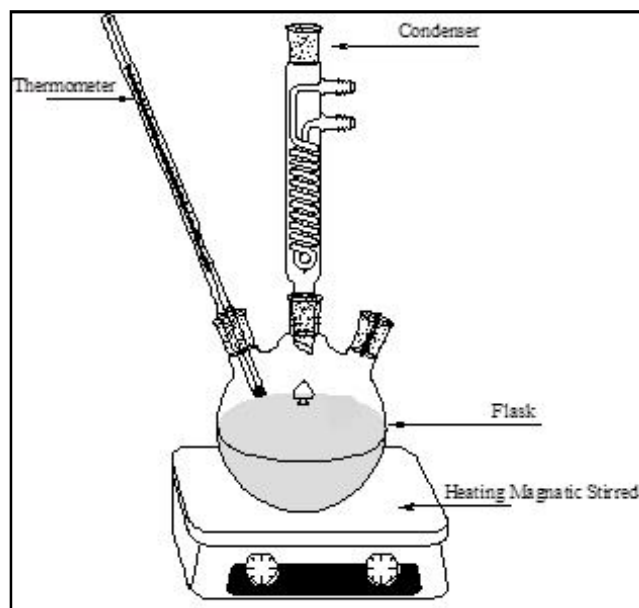

Fig. 2. Schematic diagram of the reactor

5- The slurry of product was crystallized at temperature (100°C) for (48) hours in a programmatic electrical furnace.

6- The mass of crystalline many times washed with water until pH reaching to (11.7).

7- The mass of crystalline of step 6 was dried at temperature (100°C) for (16) hours using furnace of programmatic electrical. The produced powder is NaY zeolite.

8- Copper loaded by dry-impregnation method for the produced catalyst with 10% by weight. In this technique, the effective metal ($CuCl_2$) is dissolved in water. After that, the metal including solution is added to a catalyst support including the same volume of pore as the volume of solution that was added. After that, the loaded catalyst was dried overnight at 40°C.

Esterification of oleic acid

The reactor loaded with (30 ml) of oleic acid (maintained in water bath) was mixed with the same ethanol quantity, beginning agitation with 300 rpm to obtain a respectable mixing of the compounds and removed problems of mass transfer, preheated to 70°C and then addition a 5% weight ratio of a certain catalyst to oil. The catalyst was calcinated at 300°C for 3 hours before used in reaction to ensure dryness from any amount of undesired water.

After 1 hour, the reactant solution was centrifuged for ten minutes, to make efficient the phases separation and added two drops of indicator (phenolphthalein) and titrate with sodium hydroxide (1 molarity) in order to get conversion of oleic acid, for estimating conversion form

each catalyst, the eqn. (1) was obtained as :

$$\text{Conv.} = \frac{initial\ acid\ No. \quad organic\ layer\ acid\ No.}{initial\ acid\ No.} \quad (1)$$

The determination of acid number of oleic acid and the reaction products are carried out according to the ASTM D-664.

Test methods

XRD : X-ray diffraction

XRD was don using (XRD 6000/SHIMADZU/ JABAN) instrument.

Area of surface and volume of pore

Evaluation surface area of produced catalyst and pore volume was achieved by using (BET) procedure by Thermo-Finnegan kind instrument at Ministry of Oil/ Oil Development and Research.

Results and Discussion

XRD Analysis

The solid crystal purity will be determined by the X-ray diffraction standard pattern which can be obtained from international association of zeolite with the X-ray diffraction pattern of sample (West, 1988).

XRD pattern was estimated for Iraqi kaolin and prepared NaY zeolite as shown in Fig. 3 and Fig.4 respectively.

The lattice spacing comparison between the produced NaY zeolite and the standard faujasite-Na, shows that no significant differences between the prepare NaY and faujasite.

XRD florescent show that the ratio of silica to alumina in the produced catalyst was found equal to (2.73), this result is in a good agreement with the value of 2.6 silica to alumina ratio that mentioned by (Davis and Davis, 2003) and the value of 2.4 that reported by (Abbas and Abbas, 2013) who mentioned that the ratio of silica to alumina in NaY is about 2.4 and the value of 2.6 silica to alumina ratio that reported by (Davis and Davis, 2003). While, Na_2O content of prepared NaY zeolite was found 12.8 wt.%. This result is in agreement with That results

Table 2: Lattice spacing comparison between standard synthesis faujasite-Na and prepared catalyst.

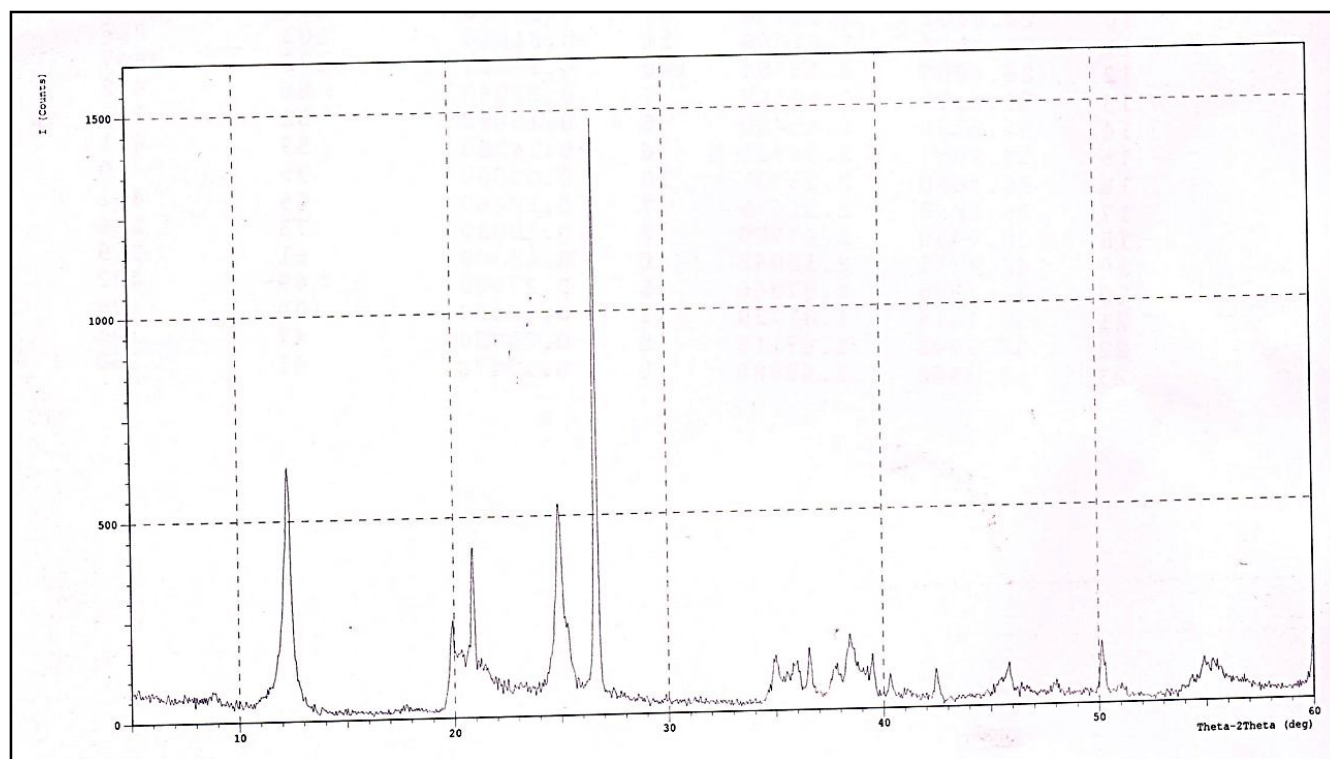| Prepared catalyst		Standard faujasite-Na	
Angle(2-Theta)deg.	d, spacing(Å)	Angle(2-Theta)deg.	d, spacing(Å)
19.28	4.60	18.65	4.36
21.65	4.10	21.80	4.07
26.69	3.34	26.64	3.30
32.20	2.78	32.04	2.7
33.80	2.65	33.56	2.66
36.15	2.48	35.90	2.53
37.70	2.38	37.72	2.4
43.68	2.07	44.36	2.04

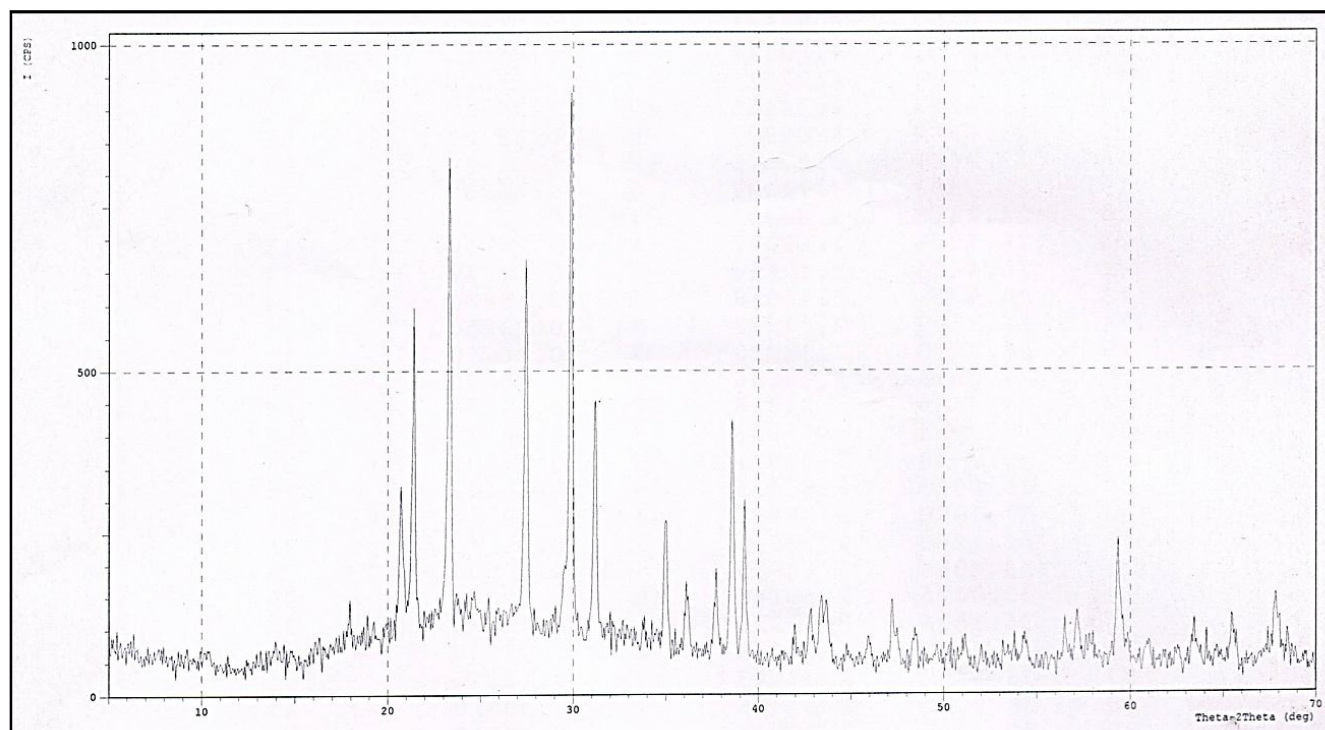**Fig. 3.** X-ray diffraction of kaolin

Fig. 4. X-ray diffraction of prepared NaY zeolite

cited by (Davis and Davis, 2003) who recorded that NaY zeolite contains approximately 12.26 and 12.50 wt.% Na_2O, respectively. Table 2 shows lattice spacing comparison between standard synthesis faujasite-Na and prepared catalyst.

Surface area

The prepared catalyst surface area was determined by physical adsorption of nitrogen at liquid nitrogen temperature by using Brunauer, Emmett and Teller (BET) method, and equal to (154 m²/gm).

The void space in the catalyst is representing the pore volume. It is determined by adsorption of nitrogen and expressed in cm³/gm.

Prepared catalysts test

The prepared NaY and promoted NaY by 10 wt % of copper, were tested as a catalyst in esterification reaction of oleic acid.

The promoted NaY recorded higher conversion of oleic acid (about 86%) at 70°C and for only one hour reaction time, while only 78 % of oleic acid was convert by aid of un-promoted NaY catalyst at same reaction conditions.

The conversion of oleic acid increasing because the increasing in the Bronsted acidity of a zeolite which is increased by increasing of copper cation loaded that balance the negative charge of the zeolite framework (Gaetan, 2013).

Conclusions

The following conclusions were obtained based on the result of this work :

1- The silica ratio to alumina is 2.73 for the prepared NaY catalyst.

2- Sodium content of the prepared NaY zeolite is 12.8 wt. %.

3- The prepared catalyst surface area is (154 m²/gm) and pore volume (0.26 cm³/gm).

4- The conversion of oleic acid increased from 78 (for prepared NaY zeolite) to 86% with used the promoted NaY zeolite catalyst at selected conditions for the esterification of oleic acid by heterogeneous catalyst after 60 minutes, 70°C and 5 wt.% of zeolite.

References

Abbas, A.S. and S.M. Abbas (2013). Kinetic Study and Simulation of Oleic Acid Esterification in Different Type of Reactors. *Iraqi Journal of Chemical and Petroleum Engineering*, 14 No. **2:** 13- 20.

Al Zuhair, S. (2007). Production of biodiesel: possibilities and challenges. *Biofuels Bioproduct and Biorefining*, **1:** 57–66.

Basha, S.A. and K.R. Gopal (2012). A review of the effects of catalyst and additive on biodiesel production, performance, combustion and emission characteristics. *Renewable and Sustainable Energy Review*, **16:** 711–717.

Bell R.G. (2001). "What are Zeolites".

Canakci, M., J. Van Gerpan (2011). "Biodiesel production from oils and fats with high free fatty acids." *Trans ASAE*, **44:** 1429–36.

Cardoso, A.L., S.C.G. Neves and M.J. da Silva (2008). Esterification of oleic acid for biodiesel production catalyzed by $SnCl_2$: A Kinetic investigation.

Chorkendroff, J.W. (2003). A book of Concepts of modern catalysis and kinetics, WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim, ISBN: 3-527-30574-2.

Davis, M.E. and R.J. Davis (2003). Fundamentals of Chemical Reaction Engineering. McGraw Hill, Boston, 166-170.

De Vrije T., G.G. de Haas, G.B. Tan, E.R.P. Keijsers and P.A.M. Claassen (2002). Pretreatment of Miscanthus for hydrogen production by *Thermotoga elfii*. *Int. J. Hydrogen Energy*, **27:** 1381–1390.

De Vrije T. and P.A.M. Claassen (2003). Dark hydrogen fermentations, in Bio-methane & Biohydrogen, J. H. Reith, R.H. Weiffels and H. Barten (eds.), Smiet Offset, The Hague, 103–123.

Dizge, N., C. Aydiner, D.Y. Imer, M. Bayramoglu, A. Tanriseven and B. Keskinler (2009). Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. *Bioresour Technol.*, **100:** 1983–91.

Dossin, T.F., M.F. Reyniers, R.J. Berger and G.B. Marin (2006). Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. *Appl. Catal. B: Gen.*, **67:** 136–148.

EWEA (European Wind Energy Association) (2005). Large scale integration of wind energy in the European power, Issues and recommendations, Brussels.

Gaetan, L. (2013). Comparison of different types of zeolits used as solid acid catalysts in the transesterification reaction of jatropha type oil for biodiesel production. A thesis submitted to the Faculty of the Worcester polytechnic institute.

Hala, K. (1971). New hydrogenation catalysts, urushibara catalyst. John Wiley, New York.

Hameed, B.H., L.F. Lai and L.H. Chin (2009). Production of biodiesel from palm oil (*Elaeis guineensis*) using heterogeneous catalyst: an optimized process. *Fuel Process. Technol.*, **90:** 606–610.

Hilditch T.P. and C.C. Hall (1937). Catalytic process in applied chemistry, Van nostrand company, New York.

Islam, A., Y.H. Taufig-yap, C. Chu and E. Chan (2013). Studies on design of heterogeneous catalysts for biodiesel production. *Process Safety and Environmental Protection*, **91:** 131–144.

Islam, R., N. Cicek, R. Sparling and D. Levin (2006). Effect of substrate loading on hydrogen production during anaerobic fermentation by Clostridium thermocellum.

27405, *Appl. Microbiol. Biotechnol.*, **72:** 576–83.

Juan, J.C., D.A. Kartika, T.Y. Wu and T.Y.Y. Hin (2011). Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: an overview. *Bioresource Technology*, **102:** 452–60.

Karmakar, A., S. Karmakar and S. Mukherjee (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, **101:** 7201–7210.

Mat, R., R.A. Samsudin, M. Mohamed and A. Johari (2012). Solid Catalysts and Their Application in Biodiesel Production. **7:** (2), 142-149.

Math, M.C., S.P. Kumar and S.V. Chetty (2010). Technologies for biodiesel production from used cooking oil – a review. *Energy for Sustainable Development*, **14:** 339–45.

Mbaraka, I.K. and B.H. Shanks (2006). Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. *J. Am. Oil Chem. Soc.*, **83:** 79–91.

McNeff, C.V., L.C. McNeff, B. Yan, D.T. Nowlan, M. Rasmussen, A.E. Gyberg, B.J. Krohn, R.L. Fedie and T.R. Hoye (2008). A continuous catalytic system for biodiesel production. *Appl. Catal.*, **343:** 39–48.

Meher, L.C., D.V. Sagar and S.N. Naik (2006). Technical aspects of biodiesel production by transesterification: a review. *Renew. Sustain. Energy Rev.*, **10:** 248–268.

Minnan L., H. Jinli, W. Xiaobin, X. Huijuan, C. Jinzao, L. Chuannan, Z. Fengzhang and X. Liangshu (2005). Isolation and characterization of a high H2-producing strain *Klebsiella oxytoca* HP1 from a hot spring. *Res. Microbiol.*, **156:** 76–81.

Mushrush, G., E.J. Beal, G. Spencer, J.H. Wynne, C.L. Lloyd, J.M. Hughes, C.L. Walls and D.R. Hardy (2001). An environmentally benign soybean derived fuel as a blending stock or replacement for home heating oil. *Journal of environmental science and health, part A: toxic/ hazardous substances and environmental engineering*, **36:** 613–622.

Serio, M.D., R. Tesser, L. Pengmei and E. Santacesaria (2008). Heterogeneous catalysts for biodiesel production. *Energy Fuels*, **22:** 207–217.

Sharma, Y.C., B. Singh and J. Korstad (2011). Latest developments on application of heterogenous basic catalysts for an efficient and ecofriendly synthesis of biodiesel: a review. *Fuel*, **90:** 1309–24.

Singh, Chouhan A.P. and A.K. Sarma (2011). Modren heterogeneous catalysts for biodiesel production: A comprehensive review. *Renewable and sustainable energy review*, **15:** 4378–4399.

Smith, J.V. (1976). Origin and Structure of Zeolites in J.A. Rabo, Zeolite Chemistry and Catalysis, ACS Monograph 171 (Amer Chem. Soc. Washington D.C.) p.3.

Soelaret, W. and E.J. Vandamme (2009). book of "Biofuels". John Wiley and Sons Ltd. ISBN: 978-0-470-02674-8.

Sonntag, N.O.V. (1979). Structure and composition of fats and oils. In: D. Sweeern, (Ed.), Bailey's Industrial Oil and Fat Products, 1, fourth ed. John wiley and Sons, New York, 1.

Taguchi, F., N. Mizukami, K. Hasegawa and T. Saito-Taki (1994), Microbial conversion of arabinose and xylose to hydrogen by a newly isolated *Clostridium* sp. No. 2, *Can. J. Microbiol.*, **40:** 228–233.

Van Andel, J.G., G.R. Zoutberg, P. M. Crabbendam and A.M. Breure (1985). Glucose fermentation by Clostridium butyricum grown under a self-generated gas atmosphere in chemostat culture, Appl. *Microbiol. Biotechnol.*, **23:** 21–26.

Vicente, G., M. Martinez and J. Aracil (2004). Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour. Technol.*, **92:** 297–305.

Viriya-empikul, N., P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop and K. Faungnawakij (2010). Waste shells of mollusk and egg as biodiesel production catalyst. *Bioresource Technology*, **101:** 3765–7.

Wang, Y., X. Wang, Y. Liu, S. Ou, Y. Tan and S. Tang (2009). Refining of biodiesel by ceramic membrane separation. *Fuel Process Technol.*, **90:** 422–7.

Wang, Y., S. Ou, P. Liu and Z. Zhang (200). Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy conversion and management*, **48:** 184–188.

Weitkamp, J. Catalysis and Zeolites (1999). Fundamentals and applications.

West, A.R. (1988). Basic Solid State Chemistry. New York: JohnWiley and Sons Inc.

Zabeti, M., W.M.A.W. Daud and M.K. Aroua (2009). Activity of solid catalysts for biodiesel production: a review. *Fuel Processing Technology*, **90:** 770–7.

Zhang, Y., M.A. Dube, D.D. McLean and M. Kates (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour. Technol.*, **89:** 1–16.

Zubir, M.I. (2009). Esterification of Oleic Acid with Ethanol by Using Tungstated Zirconia: Kineric and Modeling Study. Thesis, University of Malaysia Pahang.